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Broad-band dielectric response of $PbMg_{1/3}Nb_{2/3}O_3$ relaxor ferroelectrics: Single crystals, ceramics and thin films

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Abstract

Data of the extensive study of dielectric response of relaxor $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) single crystals, ceramics (standard and textured) and thin films (thickness 500 nm, sapphire substrate) in the broad frequency range (3×10^{-3} to 10^{14} Hz) were combined, summarized and analyzed. Influence of the mesoscopic structure, possible strain and defects in ceramics and thin film on both relaxational and phonon dynamics is discussed. The phonon response of PMN single crystal and thin film appears to be very similar, including the soft mode behaviour. Similar to PMN crystals, the dielectric response of PMN ceramics and films is mainly determined by relaxational dynamics of polar nanoclusters. Flipping and breathing of the clusters are assumed to be the dominant mechanisms, which can be resolved in the frequency spectra of the complex permittivity. The mesoscopic structure and defects in the ceramics do not result in any significant contribution to additional mechanisms, but influence the dynamics of nanoclusters and lead to pinning of the flipping contribution. In thin films the dielectric response due to cluster dynamics is much more reduced.

Keywords: Dielectric properties; Spectroscopy; Relaxor ferroelectrics; Grain boundaries; Films

1. Introduction and samples

The dielectric properties of the model relaxor ferroelectric lead magnesium niobate $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) were widely investigated during last 45 years, mainly in the low-frequency range,[1,2] but also at high frequencies and microwaves.[1,3–7] Our recent studies of the THz and infrared (IR) dielectric response of PMN single crystals[6] and thin films[8] proves that both lattice vibrations and relaxational dynamics play a fundamental role. The dynamics of polar nanoclusters, related to the structural disorder, is considered to be responsible for the relaxor behaviour and determines the dielectric response of PMN crystals.[6,9,10] In the case of ceramics and thin films, the mesoscopic structure and imperfections (grain boundaries, presence of amorphous or another second phase, etc.) or influence of the substrate and surface layers should be taken into account in addition to the structural (compositional) disorder, characteristic for the crystals. The factors mentioned above can, in principle, provide additional contributions to the dielectric response and influence the dynamics of both polar nanoclusters and crystal lattice, modifying the contributions characteristic for the single crystals. This motivated us to combine the results of our extensive study of the dielectric response of PMN single crystals,[4,6,11] ceramics[7] and thin films[8] for comprehensive analysis.

The difference in the geometry of bulk and thin film samples results in different experimental methods used and consequently in extension of the temperature and frequency ranges of investigation. The variety of experimental methods used, including infra-low-frequency,[11] low- and high-frequency[6] dielectric spectroscopy, microwave measurements,[4] time-domain THz spectroscopy[6,8] and IR reflectivity[6] and transmission[8] spectroscopy, allow us to cover almost the full frequency range (3×10^{-3} to 10^{14} Hz) and study both relaxational and phonon dynamics and their temperature evolution from 10 K to 900 K, i.e. below and above the Burns temperature, including the non-ergodic frozen phase. In this paper we discuss results, obtained on the following PMN samples prepared by different processing technologies:

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(a) Single crystals. For details of sample preparation see refs.[4,6,11]

(b) Standard and textured ceramics.[7] Standard ceramic was hot-pressed at 900 °C and then sintered at 1200 °C. The textured ceramic was made up of thick-film layers. The 100 μm thick films were prepared by rolling a mixture of fine PbO and $MgNb_2O_6$ powders at 200 °C and then stacking them into multilayer bulk samples with a thickness of about 7 mm. The bulk textured sample was hot-pressed at 900 °C and then sintered at 1200 °C. Both standard and textured ceramics contain a small quantity of a second non-perovskite phase (probably pyrochlore phase); nevertheless, they satisfy the goal of our study, to assess the influence of the mesoscopic structure, additional imperfections and inhomogeneities on the dielectric response. Three kind of ceramic samples were investigated. Ceramic 1 and Ceramic 2 samples were prepared from the textured PMN ceramics providing the direction of the measuring electric field along and across the film layers, respectively. Ceramic 3 was prepared from the standard PMN ceramics.

(c) Thin film prepared by chemical solution deposition on sapphire substrate.[8] The 500 nm thick film was polycrystalline with a predominately (1 1 1) out-of-plane orientation and a grain-size of 60 nm.

2. Relaxor behaviour of PMN crystals, ceramics and thin films

The dielectric response of all investigated ceramic samples are similar to that of PMN crystals[6,7] and show a typical relaxor behaviour (see Figs. 1 and 2). Diffuse peaks of the real and imaginary parts of the complex dielectric permittivity $\varepsilon'(T)$ and $\varepsilon''(T)$ move towards higher temperatures on increasing frequency. Dielectric dispersion takes place in a broad temperature region both below and above the temperature of permittivity maximum T_m. Relaxor behaviour was observed also in the low-frequency in-plane dielectric response of the PMN thin film,[8] as well as in the out-of-plane or parallel plate capacitor configurations.[12] A comparison of dielectric data obtained for single crystal, ceramics and thin film (Fig. 3) shows only quantitative, not qualitative differences. The main difference is in absolute values of dielectric parameters. The relative permittivity value at 1 MHz in the maximum at T_m is ∼11,000 for crystals, ∼8000 for ceramics ∼2000 for the film. The same is valid for the dielectric loss: highest loss was observed in crystals, lowest loss in the thin film. The difference between standard and textured ceramics remains within 25%. The $\varepsilon'(T)$ maximum is more diffuse in the thin film than in single crystals. The lowest T_m is in PMN crystals, the highest one in the thin film. The difference in T_m between the film and crystal is about 50 K.

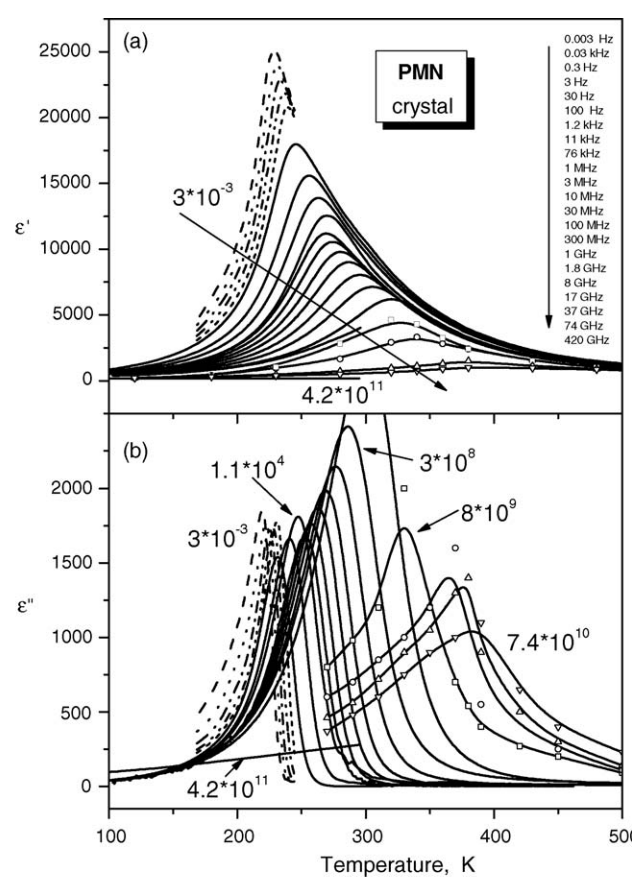

Fig. 1. Temperature dependences of dielectric permittivity ε' and loss ε'' of PMN single crystal at various frequencies. The numbers near curves denote the frequency in Hz.

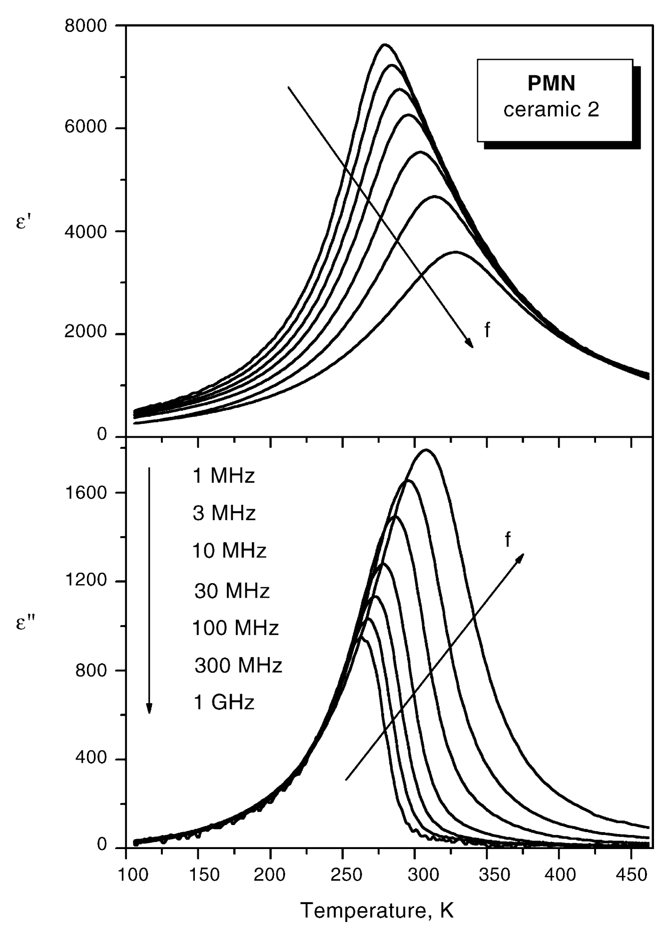

Fig. 2. Temperature dependences of dielectric permittivity ε' and loss ε'' of the textured PMN ceramic (Ceramic 2 sample) at various frequencies.